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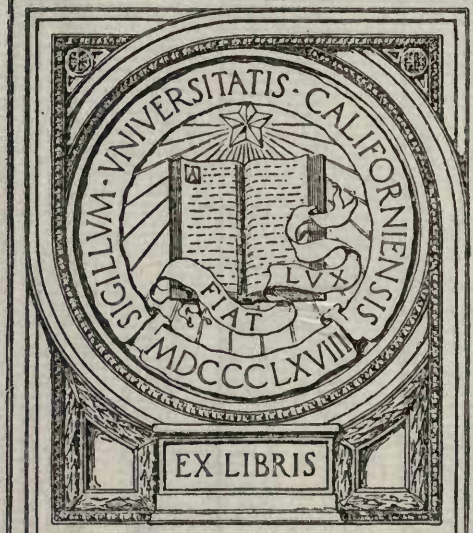
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A Comparative Study of the Slow Combustion of Methane and Methods for the Determination of its Combustion Products

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Graduate School of the Ohio State University

BY

FRANK CARL VILBRANDT, B. A., M. A.

The Ohio State University
1920

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The slow combustion methods consist in passing the combustible gas slowly into an oxidation chamber filled with oxygen or air, the combustion initiated by an electrically heated coil. The combustion pipet of Clemens Winkler (Ztsch. anal. Chem. 28, 288, 1889) was modified by the following investigators: Dennis and Hopkins (Dennis' Gas Analysis' 1913, 148), Bretschger (Treadwell-Hall. 'Quantitative Analysis', 3rd Edit. J. Wiley & Sons, p. 790), Burrell and Siebert (Bur. Mines Bull. 42, 17, 1913), Voldere (Chem. Ztg. 31, 1296, 1907), Scott (Ind. Eng. Chem. 1, 118, 1909), Burrell (U.S. Pat. 1, 176, 199, [1917]), Anderson (Ind. Eng. Chem. 11, 292, 1919) and Demorest (Private communication). The main disadvantages of this method are the incompleteness of combustion, formation of oxides of nitrogen, breakage of apparatus in the hands of non-experts and errors due to oxidation of the confining material.

The capillary method of combustion, introduced by Coquillon (Compt. rend. 85, 1106, 1877) consisted in passing a previously mixed quantity of the gas and oxygen or air through a heated platinum tube, oxidation produced only in the presence of the platinum. This apparatus was later modified by Drehschmidt (Ber. 21, 3242, 1888), Wohl (Ber. 37, 433, 1904), and Roehart (Ztsch. anorg. Chem. 38, 78, 1908); The same method modified by using quartzware instead of platinum for the capillary, but using various forms of platinum in the tube for catalysis were introduced by Sabatier ('Die Katalyse' 1st edit. Leipsig, p. 23), Wilson and Mason (Proc. Chem. Soc. [London] 21, 1296, 1905) and Mathers and Lee (Chem. Eng. 17, 159, 1913). The disadvantages in this method such as leakage of gas through hot platinum and the high cost of platinum have been fairly well taken care of in the quartz tubes.

Each modification introduced was designed to overcome some inherent error of manipulation or apparatus. The explosion method is essentially an expert's method, not capable of giving good results in other hands; the capillary method requires something better than the easily deterioratable quartz, and the slow combustion method requires the elimination of breakage due to local heating of the capillary and oxidation chamber joint, proper manipulation or apparatus design to insure completeness of combustion and the reduction of error by the use of larger quantities of gas for the combustion.

The investigation carried out primarily studied the slow combustion method with the view of eliminating the above undesirable features and to study the influence of the oxidation effects of nitrogen on the analyses when air was introduced, and to study the effects of the products of incomplete combustion of the methane.

EXPERIMENTAL

A modified Burrell common train Orsat laboratory set-up, with a Hempel temperature and pressure compensator was used. The absorption reagents used were potassium hydroxide, alkaline pyrogallate, and acid cuprous chloride, prepared according to Dennis ('Gas Analysis', 1913, pp. 160, 225, 232, 233). The methane used was prepared by the Gladstone-Tribe method (J. Chem. Soc., [London] 25, 684, 1873; 45, 154, 1883) from methyl iodide and Zn-Cu couple, but pure methane could not be made by this method. Other methods yielded no better results. Methane analysing 84.55% methane 12.10% nitrogen and 3.35% oxygen by the Dennis-Winkler method was used for the investigation.

STANDARDIZATION OF THE TEMPERATURE OF THE HEATED COIL. The references in the literature to red heat, cherry red, bright red, white heat and dull red for the temperature of the electrically heated coil was too indefinite. Following the suggestion of Burrell and Siebert (idid. p. 19) who measured the current flowing through a platinum coil, but gave no coil dimensions for reproduction of their temperatures, in this investigation, the temperatures were recorded as the amperes flowing through a #24 B. & S. gage, platinum wire, with a five millimeter diameter coil of four turns two millimeters apart.

MODIFIED ELECTRODES. Difficulties due to the use of electrodes proposed by Bretschger (loc. cit.), Dennis and Hopkins (loc. cit.) and Porter and Ovitz (Bur. Mines Bull. 1, 24, 1910) by breakage, leaks and oxidation of the mercury in the seal, led to the design of a new electrode consisting of sealed in platinum coil making contact with the current supply by means of mercury, held in the electrode tubes by rubber tube joint, with a large copper rod to which the supply wires were connected. (See [E] Figure 1.)

SLOW COMBUSTION PIPETS AND METHODS OF ANALYSIS.

In order to make a thorough survey of the difficulties inherent in each of the more modern pipets in comparison with a new proposed pipet, the following pipets and methods were studied: Dennis (ibid. p. 149) and Burrell and Siebert (ibid. p. 79). These were modified to make the Burrell and Siebert either water cooled or air cooled by providing an air jet to play against the pipet and also a continuously flowing film of water over the same. In addition the two types of pipets were supplied with the new central burner.

CENTRAL BURNER PIPET. The central burner pipet (Figure 1.) is provided with two capillary stop-cocks, B and C. Manipulation of the apparatus is carried out as follows: With C closed, air or oxygen is drawn into the pipet by lowering the mercury leveling bulb attached to the pipet at F. With ten cubic centimeters of the air or oxygen the mercury in the burner tube K is forced out by closing B and opening C. Connections are made with the supply of gas to be analysed; with the temperature of the coil attained by passing a measured current through the coil, the gas is slowly drawn into the combustion pipet by opening the stop-cock on the lowered level bulb; the gas on entering burns with a small flame at the mouth of the quartz burner tube K. When the gas has all been passed into the chamber, by manipulation of the cocks and level bulbs, about twenty cubic centimeters of the gas is withdrawn and passed back and forth into the apparatus several times to insure complete combustion of all the gas which would normally be retained in the capillary connections. This type was also supplied with water and air cooling. These pipets were constructed of transparent quartz to enable the study of cooling with water and air, not possible with glass apparatus, and to eliminate the frequent interruptions necessary to replace the easily broken glassware.

The capillary quartz tubes were of special construction, with enlarged ends to enable fitting on tubing; several different sizes were studied.

The effect of design of apparatus, reduction of apparatus temperature with water and air, effect of cutting off the current after the initiation of the combustion, the effect of varying the temperature of the platinum

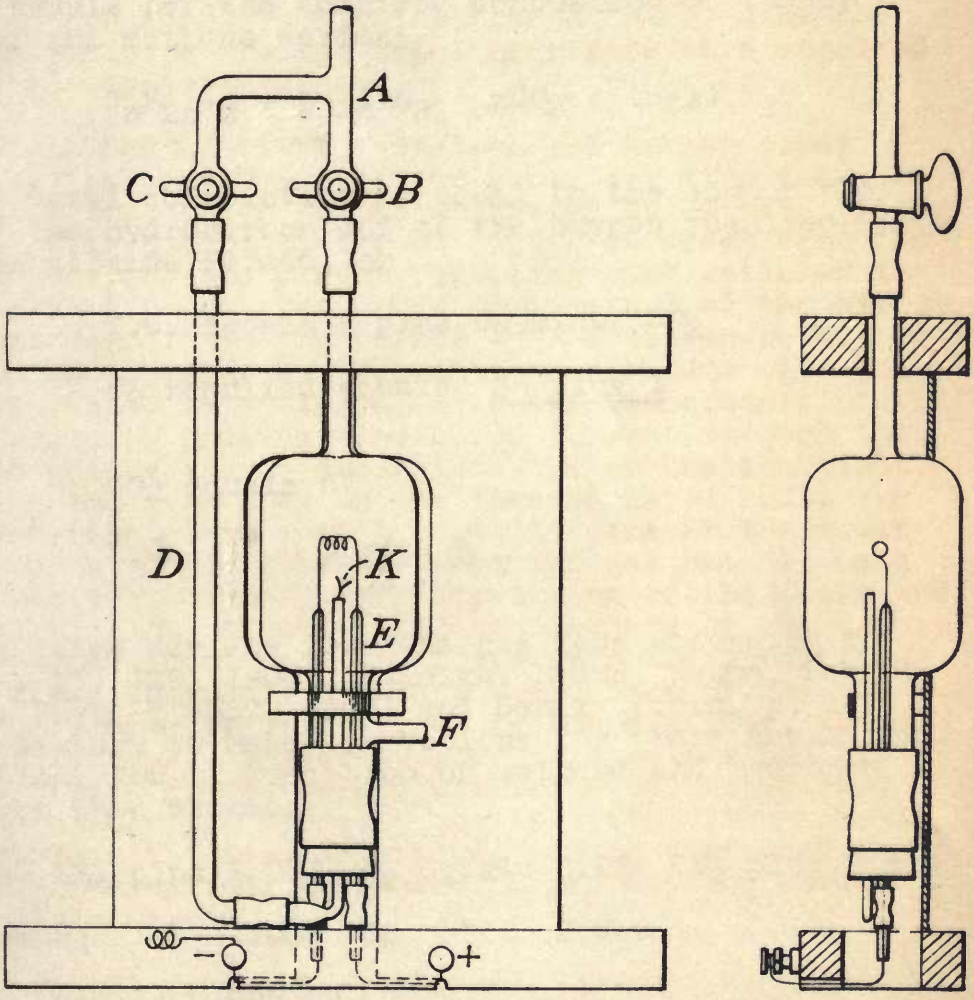
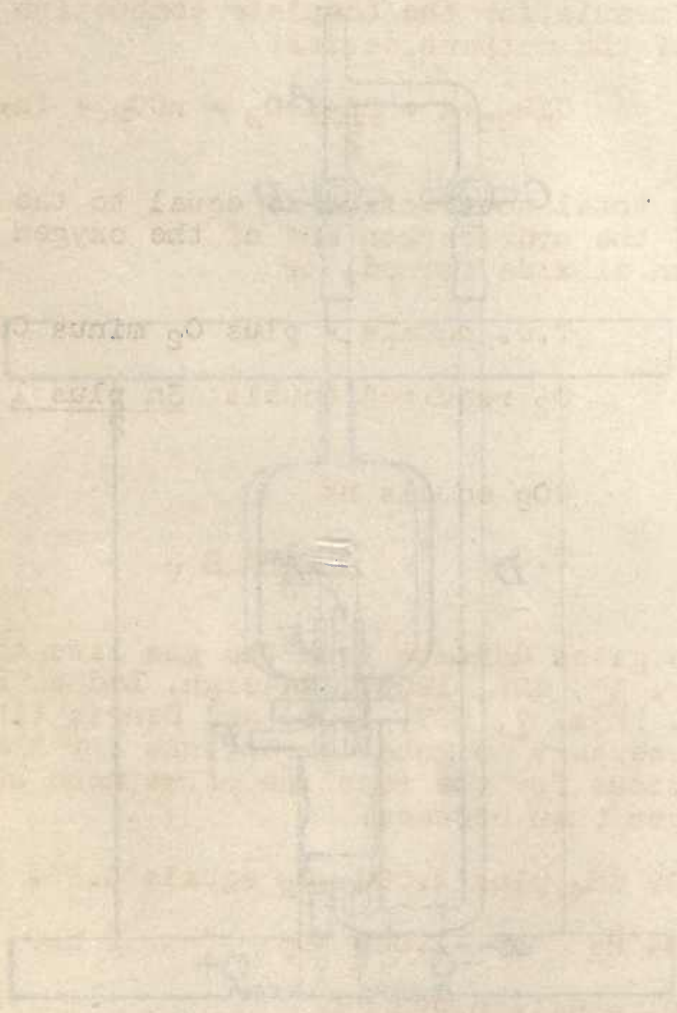


Figure I. Central Upright Burner Pipette



wire, the effect of varying the oxygen to gas ratio, the effect of rate of oxidation and presence of nitrogen were studied with the above equipment.

CALCULATIONS. The results obtained in the above study, were calculated by the use of the formulae of Voldere and De Smet (Ztsch. anal. Chem. 49, 661, 1910), Anderson (ibid. p. 302) and by the author. Using the general formula for the complete combustion of the hydrocarbons of the methane series:

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 = nCO_2 + (n+1) H_2O$$

Since the total contraction is equal to the sum of the volume of the hydrocarbon and of the oxygen required minus the carbon dioxide formed, or

T.C. equals V plus O_2 minus CO_2

then O_2 required equals $\frac{3n \text{ plus } 1}{2}$

CO_2 equals nV

T.C. " $\frac{3 \text{ plus } n}{2}$ V

Since the gases deviate from the gas laws according to Wohl (Ber. 37, 429, 1904), Raleigh, Leduc, Baume, Perrot (J. Chem. Phys. 7, 367, 1909) and Dennis (ibid. p. 139) it was necessary to make corrections for these deviations. The equations for the reaction of methane and hydrogen with oxygen then becomes:

0.999 CH_4 plus 2.000 O_2 equals 0.954 CO_2 plus 2 H_2O

2.004 H_2 " 1.000 O_2 " 2 H_2O

or, CO_2 equals 0.995 CH_4

T.C. " 1.499 H_2 plus 2.007 CH_4

In order to eliminate repeated development of correct equations on the basis of carbon dioxide remaining in the gas after combustion a correction factor was developed for the different hydrocarbon values following the plan of Anderson (ibid. p. 302)

SUMMARY OF COMBUSTION DATA. The data obtained in this investigation is compiled in Table 1, the results being averages of from three to six determinations, including all data such as type of apparatus, modification, color of heating coil, current flowing through wire, rate of gas flow, ratio of oxygen to gas sample, analyses and estimated average completeness of combustion.

DISCUSSION OF RESULTS.

FORMATION OF OXIDES OF MERCURY. Many determinations not recorded in Table 1 were eliminated because of formation of oxides of mercury due to the high local heating of parts of the apparatus in contact with the mercury containing fluid. Mercury oxidation does not affect methane percentages but, by increasing the total contraction, increases the hydrogen percentages. Two forms of the oxides of mercury were found in the pipets during some of the worthless combustions;- red and brownish yellow. The red variety occurred at high coil temperatures and the yellow at low heats.

INFLUENCE OF WIRE COIL TEMPERATURE. The results show incompleteness of combustion with the coil heated with below 6.8 amperes; additional experimentation showed that no ignition of the gases resulted when less than 6.5 ampere were used to heat the coil, consisting of four turns of #24 gage platinum wire, 2 millimeters between coils and 5 millimeter coil diameter. After initial ignition of the gas the temperature of the coil had no effect.

INFLUENCE OF RATE OF COMBUSTION. After visible combustion has once been started the rate of gas flow up to 25 cubic centimeters per minute has no effect on the analyses, except that precautions must be taken where mixtures approximating explosive proportions are used that destructive explosions do not occur.

INFLUENCE OF RATIO OF OXYGEN TO COMBUSTIBLE GAS. With ratios approximating 2.0 oxygen to 1.0 gas, or no excess oxygen, results are erratic. With 25% excess oxygen, or with ratios of 2.5 to 1.0 uniform and agreeing results were obtainable. Nothing is gained by increasing the oxygen ratio above this value.

TABLE I.

SUMMARY OF COMBUSTION ANALYSES.

Series No.	Nos. of runs.	Type of Apparatus	Modification	Color of Wire	Amperes flowing through coil.	Rate of gas flow cc/min.	Ratio of Oxygen/Methane	C_nH_{2n} 2 %	Methane %	Hydrogen %	Residual Gas %	Estimated Av. Completeness of Combustion %	Remarks
A-1	3	Central Burner	Continuous Heating	Dull Red	6.25	3	7.2	52.28	40.09	12.19	47.72	47.88	
-2	3	" "	" "	" "	"	5	4.0	63.21	60.05	3.18	46.73	71.44	
-3	3	" "	" "	" "	"	8	1.6	53.40	52.71	0.69	46.40	62.78	
B-1-a	3	Dennis-Winkler	Continuous Heating	" "	6.8	15	1.5	59.72	-----	-----	40.28	66.65	
-b	6	" "	" "	" "	"	15	2.0	80.06	-----	-----	19.94	85.29	Some HgO formed
-c	4	" "	" "	" "	"	"	2.5	85.17	85.04	0.13	14.76	100.97	
-d	5	" "	" "	" "	"	"	3.0	81.94	81.49	0.45	18.06	96.77	
-2-a	5	" "	" "	Bright	7.4	"	2.0	81.09	76.36	4.73	18.91	90.70	
-b	6	" "	" "	"	"	variable	2.5	84.08	83.82	0.26	15.91	99.62	
-c	5	" "	" "	"	"	10	3.0	84.41	84.01	0.40	15.59	99.52	
-3-a	4	" "	" "	White	8.4	15	2.0	75.02	74.25	0.77	24.98	88.05	Some HgO formed
-b	6	" "	" "	"	"	15	2.5	84.19	83.80	0.39	15.82	99.31	

TABLE I. (Cont'd)

SUMMARY OF COMBUSTION ANALYSES.

Series No.	Nos. of runs.	Type of Apparatus	Modification	Color of Wire	Amperes flowing through coil	Rate of gas flow cc/min.	Rate of Oxygen/Methane	C_nH_{2n} %	Methane %	Hydrogen %	Residual Gas %	Estimated Av. Completeness of Combustion %	Remarks
C-1-a	6	Dennis-Winkler Quartz	Continuous Heating	Dull	6.8	12	2.0	81.84	79.94	2.90	17.66	94.98	HgO Formation
-b	5	" " "	" "	"	"	Variable	2.5	84.52	83.67	0.85	15.46	99.33	
-c	3	" " "	" "	"	"	15	3.0	83.58	82.99	0.54	16.62	98.44	
-2-a	4	" " "	" "	White	8.80	"	2.5	84.52	83.75	0.77	15.46	99.36	
-b	4	" " "	" "	"	"	10	3.0	84.55	84.26	0.33	15.45	100.02	
D-1-a	4	" " "	" "	"	8.4	15	2.5	84.65	84.07	0.58	15.35	99.78	
- -b	4	" (air cooled) (" " " ")	"	"	8.8	"	2.7	84.52	84.24	0.28	15.48	99.96	
E-1-a	6	Central Burner Winkler	"	Dull	6.8	20	2.0	79.35	77.14	2.21	20.65	92.63	HgO formation
- b	4	" " "	"	"	"	Variable	2.5	84.43	83.60	0.85	15.67	99.61	
c	2	" " "	"	"	"	"	3.0	84.26	83.97	0.29	15.74	99.59	
2-a	4	" " "		Bright	7.4	20	2.5	84.18	84.01	0.17	15.82	99.71	

TABLE I. (Cont'd)

SUMMARY OF COMBUSTION ANALYSES.

Series No.	Nos. of runs.	Type of Apparatus	Modification	Color of Wire	Amperes flowing through coil	Rate of gas flow cc/min.	Ratio of Oxygen/Methane	C_nH_{2n} 2 %	Methane %	Hydrogen %	Residual Gas %	Estimated Av. Completeness of Combustion %	Remarks
b	3	Central Burner	Winkler	Bright	7.4	20	2.7	84.50	83.71	0.79	15.50	99.64	
D-1-a	4	"	"	"	"	25	2.2	84.51	83.74	0.77	15.49	99.42	
b	4	"	"	"	"	20	2.5	84.52	84.04	0.48	15.48	99.82	
c	2	"	"	"	"	"	3.0	84.48	84.05	0.43	15.76	99.77	
E-1-a	4	"	"	"	"	10	2.5	84.60	83.97	0.63	15.40	99.41	
F-1-a	4	"	"	"	(continuous and air cooled).	12	2.5	84.51	83.87	0.64	15.49	99.62	
G-1-a	4	"	"	"	"	10	2.5	84.66	83.92	0.74	15.34	99.61	
H-1-a	4	Burrell	Burrell Quartz	Cherry	7.0	10	2.5	84.44	83.86	0.58	15.56	99.58	
2-a	4	"	"	White	8.8	8	3.0	85.52	83.98	1.54	14.68	99.47	
I-1-a	3	"	Quartz (Water-cooled)	"	"	10	2.2	84.24	83.67	0.57	15.76	99.50	
2-b	3	"	"	"	"	8	3.0	84.59	84.46	0.13	12.06	100.26	
J-1-a	3	"	Air	"	"	"	3.0	85.84	84.86	0.98	10.81	100.75	

TABLE I. (Cont'd)

SUMMARY OF COMBUSTION ANALYSES.

Series No.	Nos. of runs.	Type of Apparatus	Modification	Color of Wire	Amperes flowing through coil.	Rate of gas flow cc/min.	Ratio of Oxygen/Methane	C_nH_{2n} %	Methane %	Hydrogen %	Residual Gas %	Estimated Av. Completeness of Combustion %	Remarks
K-1-a	2	Capillary	(wire inside)	Bright	Teclu Burner	18	2.2	73.93	72.51	1.42	26.07	86.07	
b	2	"	"	"	" " "	14	2.5	82.38	81.02	1.36	17.62	96.19	
c	3	"	"	"	" " "	10	3.0	85.00	83.38	1.62	15.00	99.00	
2-a	1	"	"	White	Blast	12	2.2	81.19	81.01	0.18	18.81	97.36	
b	1	"	"	"	"	10	2.5	84.39	83.92	0.47	15.61	99.63	
c	4	"	"	"	"	6	3.0	84.36	83.89	0.47	15.64	99.59	
d	2	"	"	"	"	"	4.0	84.69	84.05	0.64	15.31	99.79	
L-3-a	2	"	(foil inside)	"	"	"	3.5	84.53	83.72	0.77	15.47	99.39	
4-a	1	"	(foil outside) (wire inside)	"	"	12	2.2	80.12	80.00	0.12	19.88	94.97	
b	3	"	(" = ") (" = ")	"	"	4	2.5	84.79	84.56	0.23	15.21	99.99	

INFLUENCE OF FORM OR TYPE OF PIPET. Quartzware apparatus gave as good results as glass. The results with the new Central Burner pipet, which does away with the heating of the capillary and pipet joint, and uses the principle of burning the gas in the center of an atmosphere of oxygen, eliminating the flame front effect of the Winkler modified pipets, gave results more uniform and higher than with other pipets. Under varying conditions this form of pipet averages a completeness of combustion of 99.85% with a maximum deviation from the mean of 0.86% below and 0.92% above this figure. The Winkler modification pipet averaged 0.21% lower completeness of combustion with a deviation of 2.5% above and 5.43% below. The Burrell pipet averaged 0.33% higher with a lower limit of 1.73% and an upper limit of 1.63%. The deviations occurring in pipets other than the Central Burner occurred with variations in oxygen gas ratio, indicating a larger range with the new pipet. The results with this pipet are not affected by method of heating, rate of cooling, temperature of the apparatus and rate of gas flow up to 25 cubic centimeters per minute.

FORMATION OF OXIDES OF NITROGEN. Determination of the quantity of oxides of nitrogen with sulfanilic acid and α-naphthylamine in acetic acid solution showed increasing amounts of nitrites in the alkali with increase in oxygen excess. The temperature of the wire had no effect. However, the maximum quantity found was only 0.05 cc., the limit of accuracy in reading the Hempel gas buret. This agrees with the conclusions of Dennis (ibid) and Burrell and Siebert (ibid). The formation of oxides of nitrogen in larger quantities in the Dennis-Winkler pipet than in other types confirms the conclusions of White (J. Amer. Chem. Soc. 23, 476, 1901).

FORMATION OF FORMIC ACID AND FORMALDEHYDE. Rerun determinations as done in the oxides of nitrogen study were made to determine the amount of formic acid and formaldehyde formed during the combustion. The rosaniline hydrochloride test of Bone-Wheeler (J. Chem. Soc. London, 83, 1083, 1902) and the phloroglucinol test (Allen: Commercial Organic Analysis, Vol. VIII, p. 171) were used for formaldehyde and the modified Hauser (Chem. Ztg. 39, 57, 1915; Allen's Commercial Organic Analysis, Vol. VIII, p. 191) test was used for the detection and determination of formic acid. Only traces of formaldehyde were formed in the combustion pipets. Formic acid was also found, but in quantities which were but slightly greater than

the error in reading the buret; the largest volumes found were 0.07 and 0.068 cc. with one set of runs running 0.143 cc. The results show larger quantities formed when the ratio of oxygen to gas is low.

CAPILLARY COMBUSTION DATA.

The quartz capillary, eliminating the presence of an oxidizable confining metal mercury and giving intimate contact of the mixed gases with the catylist, gave an average estimated completeness of combustion of 99.56% with a maximum deviation from this mean of 0.79% above and 0.58% below. Increase in the rate of gas flow over the platinum decreases the completeness of combustion. The slower the rate of gas flow the lesser the number of repeated passages of the gas over the platinum to bring about complete combustion, determined by non-glowing of platinum.

DEVITRIFICATION OF QUARTZ CAPILLARY TUBES.

Fused transparent quartzware deteriorated very rapidly when gases were burned in capillaries made of this material. The devitrification initiated at points of contact of the platinum with the quartz, With the Teclu burner, only seven determinations were possible before the frosting was too prohounced to use the capillary for further work. With the blast flame directed against the outside of the capillary with platinum wire inside for the catalyst, one tube broke after the fourth run, the second tube after five runs. Using in addition to the above a platinum foil on the outside of the tube to protect it against the direct blast, nine determinations were accomplished before the tube broke. With the foil inside, seven runs was the maximum. Microscopic examination of the wires, foils and quartz tubing showed a deep checking on the quartz, and many particles of the fused quartz impinged on the wires and foils. A few crystals of quartz were also isolated, these having a greater coefficient of expansion than the fused variety, probably caused the splitting off of the latter when the tubes were subjected to changes in temperature. Fused quartz as combustion tubing in direct contact with platinum as a catalyst deteriorated too rapidly in this investigation to be accepted as a satisfactory substitute for Coquillon's platinum capillary.

CONCLUSIONS.

The investigation presents the following conclusions:

1. The development of a new type of combustion pipet, the Central Burner, which eliminates inherent errors in the construction and manipulation of other combustion pipets: results with this pipet are not appreciably influenced by rate of combustion, temperature of the coil or excess oxygen;

2. A satisfactory gas pipet electrode has been developed, eliminating troublesome mercuric oxide formation;

3. The elimination of the long capillary on the common pipets tends toward conservation of apparatus;

4. The proper excess of oxygen for combustion with the old pipets is twenty-five per cent;

5. The temperature of the heating element can be standardized by measuring the current;

6. The effect of the formation of oxides of nitrogen on the analysis is negligible;

7. The effect of the formation of formaldehyde and formic acid on the analysis is negligible;

8. Fused quartz gives more satisfactory service than glass as a material of construction for combustion pipets;

9. Capillary combustions with platinum as catalysts gives very good results, but quartz capillary does not stand up under this treatment.

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